

Dendrites in Lithium Metal Anodes: Suppression, Regulation, and Elimination

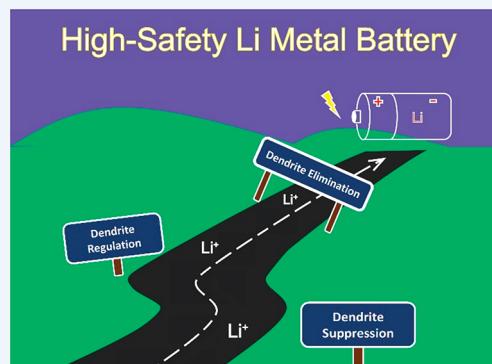
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CONSPECTUS: With the increasing diversification of portable electronics and large-scale energy storage systems, conventional lithium-ion batteries (LIBs) with graphite anodes are now approaching their theoretical limits. Lithium metal, as the “Holy Grail” electrode for next-generation rechargeable batteries, is being revisited to meet the booming demand for high energy density electrodes due to its ultrahigh theoretical specific capacity and negative redox potential. Nevertheless, typical issues like notorious dendrite growth still hamper the bulk application of Li metal anodes. Dendrite growth renders increased surface area of the lithium metal, causing persistent depletion of the electrolyte and active materials, facilitating catastrophic failure of the battery, and even inducing fatal safety hazards. The consequences become more serious during operation at high current densities and over long cycling life. Therefore, it is urgent to suppress and even eliminate dendrite formation during the Li plating/stripping process.

This Account highlights several innovative strategies for dendrite suppression, dendrite regulation, and dendrite elimination from the perspective of interface energy and bulk stresses. First, we review the fundamental mechanism of dendrite formation and growth in Li metal anodes. We show that the dendrite morphology could be substantially ameliorated, in theory, by homogenizing the electric field distribution, lowering the Li ion concentration gradient, and facilitating mechanical blocking. Next, we address the problem of dendrite suppression by applying two-dimensional (2D) materials to Li metal systems and preventing dendrite penetration through stress release and mechanical blocking. Graphene with a high specific area and vermiculite sheets (VSs) with a large physical rigidity were demonstrated to be efficacious in reinforcing Li anodes and polymer electrolytes separately. However, Li dendrite growth is a continuous process and remains inevitable with increasing current density and cycling life. Instead of suppressing dendrite growth, we focus on how to regulate homogeneous Li dendrite formation and growth. Dendrite regulation means to allow dendrite growth but take steps to transform it into Li with a smooth morphology. We introduce two main strategies to regulate Li growth: (i) guiding Li nucleation and (ii) controlling the Li growth pathways and directions. These processes greatly rely on the interface energy between the substrate and Li atoms. Elimination of the dendrites, which is the most formidable challenge for dendrite control, can also be achieved by dynamically engineering the force, such as deflecting the electric field by Lorentz force in a magnetic field, enhancing the integrated yield stress by the design of bulk nanostructured materials, and reducing the lateral Li diffusion barrier by a biomimetic co-deposition process.

Solutions to the challenges of dendrite control in Li metal anodes can provide safe next-generation rechargeable lithium metal batteries that have a long cycling life. We also hope that our strategies presented in this Account can offer promise for other metal batteries.



INTRODUCTION

With the increasing demand for state-of-the-art portable electronics, electric vehicles, and grid energy storage stations, rechargeable batteries with ultrahigh energy density and safe operation have gained increasing attention.¹ Insertion-type lithium-ion batteries (LIBs) have demonstrated great success in consumer electronic devices in the past 10 years. However, they are now approaching their energy density limit and cannot satisfy the progressive requirements of advanced energy storage applications.² Compared with commercialized LIBs, lithium metal batteries (LMBs) do not have the drawback of limited energy density and are strongly considered due to the ultrahigh theoretical capacity (3860 mAh g⁻¹) and low electrochemical

potential (−3.04 V vs the standard hydrogen electrode) of lithium metal anodes (LMAs).^{3–6} In fact, LMAs were employed in the 1970s, but they were quickly discarded owing to the ramified and tree-like morphology Li deposition, which is called dendrite in liquid electrolyte.^{7–9} The uncontrollable dendrite growth continuously consumes the active materials and punctures the separator, resulting in irreversible capacity loss, short circuits, and even safety hazards.^{10–12} The dendrite formation would become more serious under high current density and long cycling operation.

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Therefore, to unlock the full demonstration of LMBs with high energy density and safe operation, it is imperative to devote efforts in alleviating and even eradicating dendrite growth.

From this viewpoint, extensive research on the mechanism of dendrite formation and the principles of dendrite growth has been conducted.^{13–17} It was demonstrated that the dendrite morphology could be ameliorated, in theory, by homogenizing the electric field distribution, facilitating Li ion diffusion, and mechanical blocking. Many comprehensive reviews have been published focusing on strategies dealing with Li dendrites.^{18–20} The strategies are primarily investigated according to the process of dendrite evolution: (i) burgeoning, (ii) nucleation, and (iii) growth. For example, electrolyte modification with the electrolyte additives is one of the most representative methods to suppress dendrite formation from the burgeoning stage. A stable SEI can be achieved with only a small amount of additives thus promising homogeneous Li ion distribution and dead Li reduction. Scaffolds with lithophilic nucleation sites can lead to a uniform Li ion flux and nucleation morphology, facilitating smooth Li deposition and less dendrite growth. To prevent dendrite puncture, a solid state electrolyte with high modulus was finally developed to ensure safe Li metal battery cycling.

This Account discusses some innovative approaches for dendrite suppression, dendrite regulation, and dendrite elimination in our teams from the perspective of interface and bulk stresses, which have never been systematically evaluated in previous literature reports. First, suppressing dendrite growth is the simplest way to robustly force dendrites to stop growing by applying an external barrier. Two-dimensional (2D) materials with a high specific surface area, flexibility, and mechanical strength were always used in the LMB systems.²¹ For example, graphene-reinforced LMAs and vermiculite integrated polymer electrolytes were used. The suppression method is always effective when there is a small current density and low cycling capacity. However, Li dendrite formation is a dynamic process. With increasing current density and deposition capacity, it is still possible to propagate and invalidate the suppression strategy. Consequently, it is not possible to conceal dendrites once the dendrite nuclei have formed. Instead of mechanically blocking dendrite growth, we then concentrate on how to regulate dendrite formation and growth. Dendrite regulation means allowing dendrite formation and growth but homogenizing and transforming it into smooth Li. Two main strategies in regulating dendrite growth are presented as follows: (i) guiding Li nucleation and (ii) controlling Li growth pathways and directions. These processes greatly rely on the thermodynamic interface energy. Finally, eliminating dendritic Li can drastically improve the performance of LMBs. Li dendrites should be eliminated at the budding stage, which is the most formidable challenge and the ultimate goal for dendrite control. According to the stress-driven dendrite growth mechanism, dendrites can be completely avoided by regulating the surrounding force field, such as deflecting the electric field by Lorentz force in a magnetic field, enhancing the integrated yield stress by designing bulk nanostructured materials, and reducing the lateral Li diffusion barrier by an electrostatic co-deposition process. In the following sections, we will discuss some of our recent work involving dendrite suppression, dendrite regulation, and dendrite elimination.

MECHANISMS OF DENDRITE FORMATION

To date, several models (Table 1) describing dendrite formation and early dendrite growth have been proposed,

Table 1. Theoretical Models for Dendrite Formation and Corresponding Strategies

models	mechanisms	strategy	ref
space-charge model	ion diffusion and depletion	dendrite suppression	13
heterogeneous nucleation model	nuclei formation and growth	dendrite regulation	14
deposition and dissolution model	surface tension regulation	dendrite suppression	15
stress-driven model	residual stress release	dendrite elimination	16

including the space-charge model, deposition and dissolution model, heterogeneous nucleation model, and stress-driven dendrite growth model.

The space-charge model has become the most widely accepted theory to unravel Li dendrite nucleation. Chazalviel demonstrated that the occurrence of ramified dendrites was mainly caused by the formation of a space-charge layer in dilute solutions.¹⁴ The model predicts that dendrites would appear when the Li ion concentration on the surface of the electrode drops to zero under a high current density, and the initial time of dendrite growth is called Sand's time (τ) (eq 1):

$$\tau = \pi D \frac{eC_0(\mu_a + \mu_{Li^+})^2}{2J\mu_a^2} \quad (1)$$

where D is the ambipolar diffusion coefficient, e is the electronic charge, C_0 is the initial electrolyte concentration, J is the effective current density, and μ_a and μ_{Li^+} are the anionic and Li⁺ mobility, respectively. According to the model by Chazalviel, Sand's time τ empirically relies on the electron and Li ion transfer number. A prolonged Sand's time can be achieved by dissipating the effective current density (J) or accelerating the Li ion mobility (μ_{Li^+}). Therefore, strategies such as adopting 2D material-reinforced structured anodes with relatively high specific area and electrolytes with high Li ion transfer number can be promising in inhibiting dendrite formation.

The heterogeneous nucleation model mainly focuses on the initial nucleation process. Ely and García investigated the heterogeneous nucleation process with the assistance of theoretical simulations and divided the nucleation behavior into five regimes: a nucleation suppression regime, a long incubation time regime, a short incubation regime, an early growth regime, and a late growth regime.¹⁵ The embryos formed in the nucleation regime tended to dissolve into the electrolyte and became thermodynamically stable if there was a long incubation time. A short incubation time promoted nuclei growth and prepared for the formation of thermodynamically and kinetically stable Li nuclei. Based on this model, Li dendrite growth could be controlled and even regulated to form a planar morphology by tuning the Li nucleation.

The deposition and dissolution model revealed that the dendrites originated from mechanical stress.¹⁶ The relation between the pressure difference (ΔP), surface tension (γ), and orthogonal curvature radius (R_1, R_2) in this model can be formulated as a Laplace's equation (eq 2):

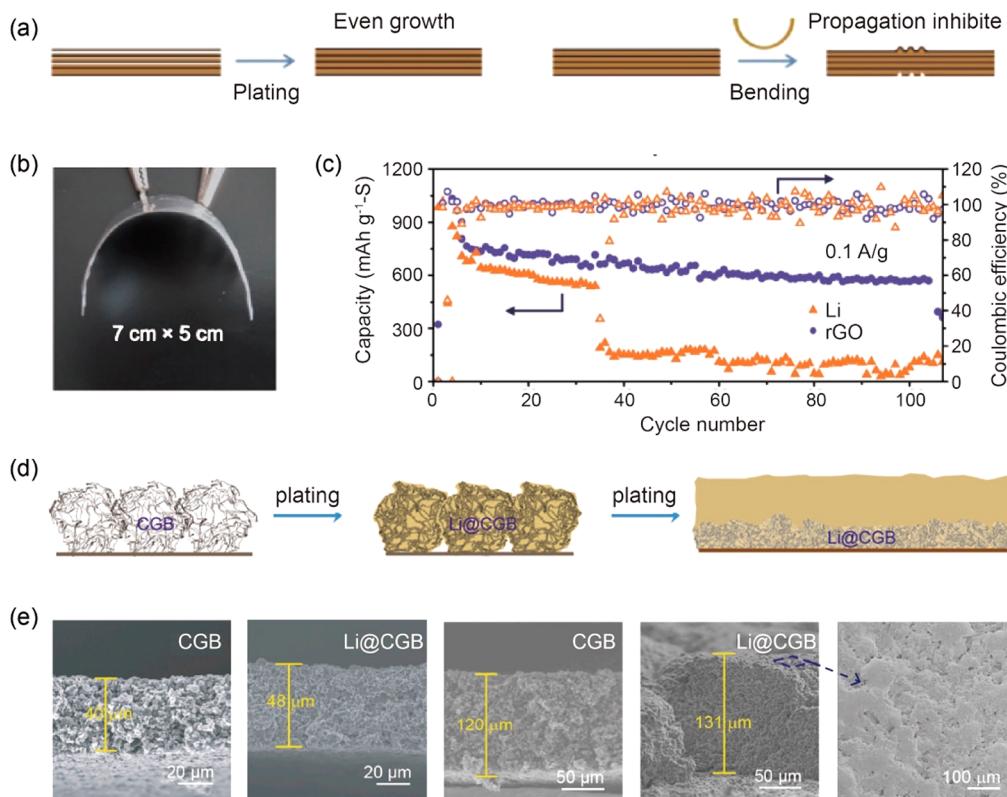


Figure 1. Dendrite suppression through 2D material-reinforced anode. (a) rGO sheets prevent Li dendrite growth even in the bending state. (b) Optical photograph and (c) cycling performance of Li–S pouch cells ($7\text{ cm} \times 5\text{ cm}$) with pure Li and r-GO/Li as the anode under the bending state. Reproduced with permission from ref 24. Copyright 2018 Wiley. (d) Schematic illustration of cGB electrodes accommodating Li deposition and dendrite growth. (e) Thickness variation of $40\text{ }\mu\text{m}$ thick and $120\text{ }\mu\text{m}$ thick cGB electrodes after plating 3.75 and 10 mAh cm^{-2} Li and surface morphology of $120\text{ }\mu\text{m}$ thick cGBs after plating 10 mAh cm^{-2} Li. Reproduced with permission from ref 26. Copyright 2018 Elsevier.

$$\Delta P = \gamma(1/R_1 + 1/R_2) \quad (2)$$

Based on this model, Yamaki et al.¹⁶ demonstrated that a “hard film” with surface tension above 0.2 N m^{-1} can serve as a protective layer and mechanically block dendrite penetration.

Recently, Jiang et al. put forward a stress-driven dendrite growth model and identified that the dendrites may arise from the residual stress during Li plating and stripping.¹⁷ It points out that dendrites would be initiated when the filament growth rate, ν_{filament} , is larger than the homogeneous plating rate, ν_{plating} ($\nu_{\text{filament}} > \nu_{\text{plating}}$), and ν_{filament} is related to the compressive stress (eqs 3 and 4):

$$\nu_{\text{plating}} = jV_{\text{Li}}/F \quad (3)$$

$$\nu_{\text{filament}} = D_{\text{Li}} V_{\text{Li}} \sigma / RTr \quad (4)$$

where j is the plating current density, V_{Li} is Li molar volume, F is Faraday’s constant, D_{Li} is the effective Li diffusivity in the Li layer, σ is the compressive stress, and r is the filament radius. According to the model, a stress-relieving mechanism can be utilized to direct desirable dendrite-free Li plating in LMAs.

■ APPROACHES FOR DENDRITE SUPPRESSION

2D-Material-Reinforced Li Metal Anodes

The space-charge, deposition, and dissolution models presented above highlight the importance of dendrite suppression in achieving a safe LMA, which inspired us to suppress dendrite formation and subsequent growth. To dissipate the effective deposition current densities (μ_{Li^+}) and

release the surface tension (γ), 2D materials were integrated into LMAs.

Graphene-based anodes are the most comprehensively investigated materials for hindering filament growth.^{22,23} Previously, Wang et al. fabricated r-GO/Li composite film anodes by capillary infusion of molten Li into r-GO interlamination.²⁴ The r-GO scaffolds with large surface areas were nonreactive, bendable, highly conductive, and mechanically stable, thus leading to a decreased electrical current density and releasing the bending stress during Li plating/stripping (Figure 1a). The plating/stripping process would always take place under the r-GO sheets that served as physical blocks and helped to suppress dendritic Li formation and growth even in the bent state. Li–S pouch cells that were bent to 180° were tested with pure Li and r-GO/Li as anodes (Figure 1b). The pouch cell with the r-GO/Li anode could run for over 100 cycles, while only 35 cycles were possible for pure Li due to the local dendrite penetration (Figure 1c).

However, Li metal is a “hostless” material, and the anode would always suffer huge volume fluctuations, causing cracks in the battery configuration, finally short-circuiting the battery.²⁵ Therefore, 3D crumpled graphene balls (cGBs) with high external/internal surface area, high mechanical stress resistance, and paper ball-like hollow structure were demonstrated (Figure 1d).²⁶ cGBs are typically synthesized through the isotropic capillary compression method, in which the sub-micrometer-sized particles tend to be aggregation-resistant. Continuous cGB electrodes with smooth surface can be assembled to accommodate a large amount of Li plating; for

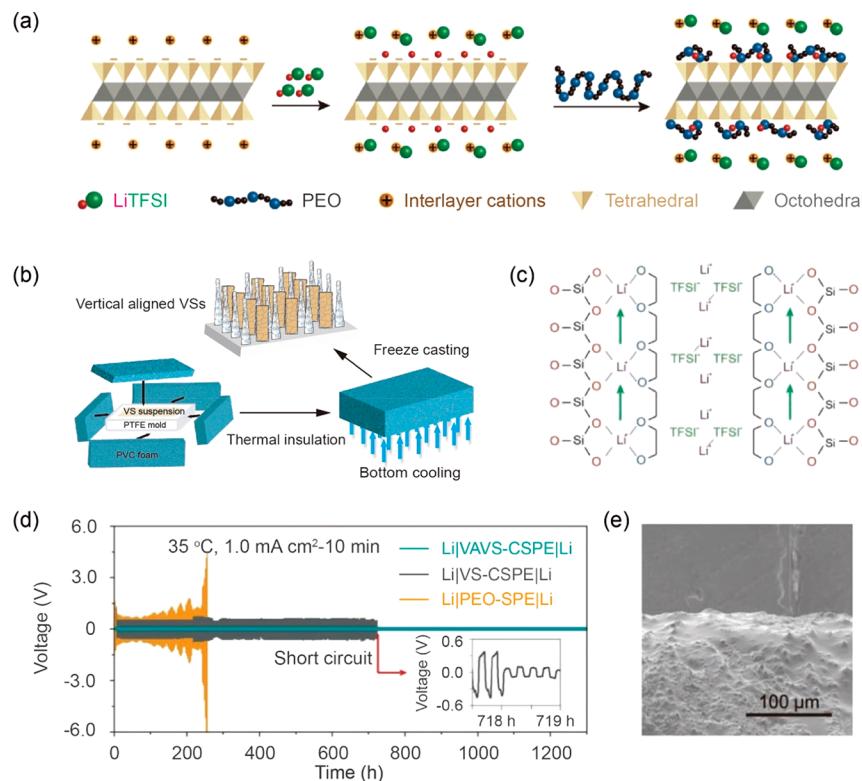


Figure 2. Dendrite suppression through solid electrolyte filled with 2D materials. Schematic of (a) enhanced ionic conductivity of PEO polymer electrolyte composite with 2D VSs. Reproduced with permission from ref 30. Copyright 2018 Wiley. Schematic of (b) fabrication of VAVSs and (c) Li^+ transport mechanism in VAVS-CSPE. (d) Galvanostatic cycling performance of symmetric cells with different types of solid electrolytes at a current density of 1 mA cm^{-2} . (e) Nondendrite Li electrode surface morphology after cycling with VAVS-CSPE electrolyte. Reproduced with permission from ref 34. Copyright 2019 Wiley.

example, 3.75 and 10 mAh cm^{-2} of Li can be well accommodated into the cGB electrodes with electrode thicknesses of 48 and $131 \mu\text{m}$, respectively (Figure 1e). Nondendritic morphology was observed after depositing 10 mAh cm^{-2} Li, which is mainly ascribed to the dissipated current density, decreased mechanical stress, and confined hollow volumes.

To sum up, dendrites could be mechanically suppressed with the assistance of 2D material-reinforced anodes.

2D Sheet Filler Enhanced Solid-State Electrolytes

In addition to anode amelioration, modification of the electrolyte is also a good method for impeding dendrite propagation.^{27–29} It has been demonstrated that dendrites can be suppressed when the shear modulus of the separator (approximately 6 GPa) is 1.8 times higher than that of Li metal (4.9 GPa). As a consequence, it is imperative to develop a solid electrolyte with a modulus exceeding that of Li. Solid-state electrolytes (SSEs) are categorized into inorganic ceramic electrolytes and solid polymer electrolytes (SPEs). The former possesses a relatively high room temperature ionic conductivity, but the stiff rigidity and brittle friability result in deficient contact with the Li anode. In contrast, SPEs combined with Li salt are stretchable, flexible, and compatible with Li anodes but negatively impact the ionic conductivity and mechanical strength. Extensive efforts have been devoted to incorporating inorganic fillers into polymer matrices, hence improving ionic conductivity and mechanical strength.

Compared to zero-dimensional (0D) nanoparticles and one-dimensional (1D) nanowires, 2D materials have a relatively high surface area that could increase the active interface with

the polymer and prevent matrix deformation under external forces, thus collectively enhancing the ionic conductivity and mechanical strength. Tang et al. proposed a 2D material upgraded with a SPE by combining 2D vermiculite sheets (VSs) as fillers.³⁰ VSs are similar to inactive ceramic fillers in some aspects, such as the chemical inertia, thermal stability, mechanical robustness, and, especially, the low cost and processability. Each layer of the VSs herein consisted of a Mg-based octahedral sheet sandwiched between two Si-based tetrahedral sheets (Figure 2a). The Si atoms were partially substituted by Al atoms, thus inducing a negatively charged surface, which is critical for facilitating Li salt dissociation and Li^+ transport. Simultaneously, dendrite growth can be effectively suppressed by a mechanical resistance due to the high Young's modulus of 175 GPa of VSs. The flame retardant capability of composite SPEs is also enhanced because of the high thermal stability of the VS fillers, which provides a significant safeguard for all-solid-state Li metal batteries.

High ionic conductivity must also be provided along with an acceptable safety level, chemical stability, thermal stability, and mechanical strength. Randomly distributed fillers in SPEs disrupt the Li^+ pathways and junctions, leading to limited utilization and conductivity.³¹ Oriented and aligned nanoparticles or nanowires were explored to produce fast Li^+ conduction without disrupting the ion transport pathways.^{32,33} Further, we demonstrate that vertically aligned 2D fillers would be more efficient than other orientations of 2D fillers in SPEs with a unique plane-to-plane conduction.³⁴ Vertically aligned vermiculite sheets (VAVSs) were fabricated through the temperature gradient freezing method (Figure 2b). Cations

were electrostatically attracted to the surface of the VSs and the aligned, consecutive, and run-through polymer–filler interfaces contributed to fast Li ion transport (Figure 2c). The symmetric cell performance of VAVS-CSPE at the current density of 1 mA cm^{-2} showed excellent cycling stability in terms of both the hysteresis and lifespan (Figure 2d), and no dendrites were obtained after cycling for the Li anodes from Li|VAVS-CSPE|Li cells (Figure 2e).

Thus, a solid-state electrolyte plays an important role in suppressing dendrite growth and provides an approach for highly safe all-solid-state Li metal batteries.

■ APPROACHES FOR DENDRITE REGULATION

Dendrite suppression by prolonging the Sand's time or physically blocking them is always an effective strategy in the case of a small current density and low cycling capacity.³⁵ However, Li dendrite formation is a kinetically and thermodynamically favorable process, and it is still highly possible to propagate under high mass loadings and current densities, thus invalidating the suppression strategy.^{36,37} Therefore, we focused on how to regulate dendrite formation and growth. Dendrite regulation means allowing dendrite formation and growth but trying to control the dendrite nucleation sites, electric field distribution, and ion transport directions to achieve a bulk Li layer with smooth surface. Two main representative strategies to guide dendrite growth are introduced as follows: (i) regulating Li nucleation and (ii) controlling Li growth pathways and directions.

Regulating Li Nucleation Sites

Li nucleation is a critical factor for Li dendrite growth. Once Li nuclei are established, Li ions prefer to deposit on these active sites due to the decreased deposition interface energy. Liu et al. modified a commercial Cu current collector by magnetic sputtering of a Cu₉₉Zn alloy layer on it (Figure 3a).³⁸ The Li⁺ flux concentrated around defects on the commercial Cu current collector, while uniformly distributed Cu₉₉Zn heterogeneous seeds generate homogeneous Li plating due to the expected nucleation. Filament dendrites were observed under a small capacity of 0.1 mAh cm^{-2} for the Cu current collector, and microparticles became connected for the Cu₉₉Zn-decorated current collector. Pancake-like bulk Li without dendrites was finally obtained under high loadings of 0.5 and 1 mAh cm^{-2} (Figure 3b). However, the chemical constitution and contents of the artificial defects still need to be further investigated and optimized.

In fact, Li deposition that occurs on itself has a very low nucleation overpotential and interface energy that could help to ensure even Li growth. A horizontal centripetally grown LMA that utilized the autologous nucleation approach was reported. The centripetally grown LMAs were achieved by compositing Li and patterned reduced graphene oxide (rGO) films (P-rGO). Due to the unfavorable nucleation on the top surface of the rGO, the electric field distribution in the voids was moved to the edges of the P-rGO along with the metallic Li (Figure 3c).³⁹ The dendrite growth was thus guided to the horizontal centripetal direction, where the dendrites finally blended with each other and filled the empty voids. Stable cycling with a small hysteresis was obtained even under a high current density of 10 mA cm^{-2} , which was among the highest value obtained herein for LMAs (Figure 3d).

Regulating Li nucleation sites with low interface energy and Li wetting capability is pivotal for regulating dendrite

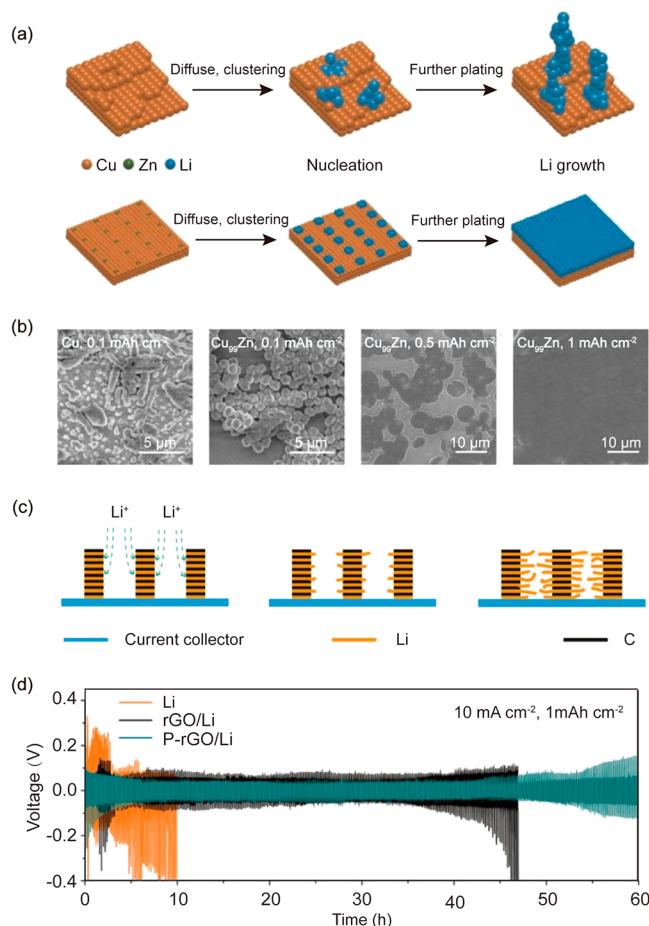


Figure 3. Dendrite regulation by controlling Li nucleation sites. (a) Schematic showing the Li plating process on Cu- and Cu₉₉Zn-modified substrates with lower deposition interface energy. (b) Li plating morphology on Cu substrate under the deposition capacity of 0.1 mAh cm^{-2} and Cu₉₉Zn-modified substrates under the deposition capacity of 0.1 , 0.5 , and 1 mAh cm^{-2} . Reproduced with permission from ref 38. Copyright 2018 Elsevier. (c) Transverse dendrite growth under the direction of the electric field. (d) Symmetric cell cycling performance of P-rGO/Li at a current density of 10 mA cm^{-2} under a deposition capacity of 1 mAh cm^{-2} . Reproduced with permission from ref 39. Copyright 2018 Elsevier.

formation and growth, which needs to be highlighted to produce very safe LMAs.

Controlling Li Growth Pathways and Directions

For 3D scaffolds, the current density can be decreased, and the volume fluctuation could be mitigated owing to its high surface area and porous structure. Uniform nucleation can also be achieved by introducing lithophilic functional groups. However, scaffolds can be divided into insulating/ion-conducting matrices and electron conducting matrices. Regardless of how uniformly the nucleation sites are distributed, Li as the exclusive electron conductor would become disconnected in single ion conductive scaffolds. In contrast, the Li ion stripping process would be greatly limited in the electronically conductive skeleton, causing insufficient Li replenishment and a disorganized and unoriented ion flux under high current densities. Based on this notion, creating a mixed ionic and electronic conductor (MIEC) composite scaffold is urgently needed to control Li ion pathways and dendrite growth directions under high-rate operation.^{40–42} It

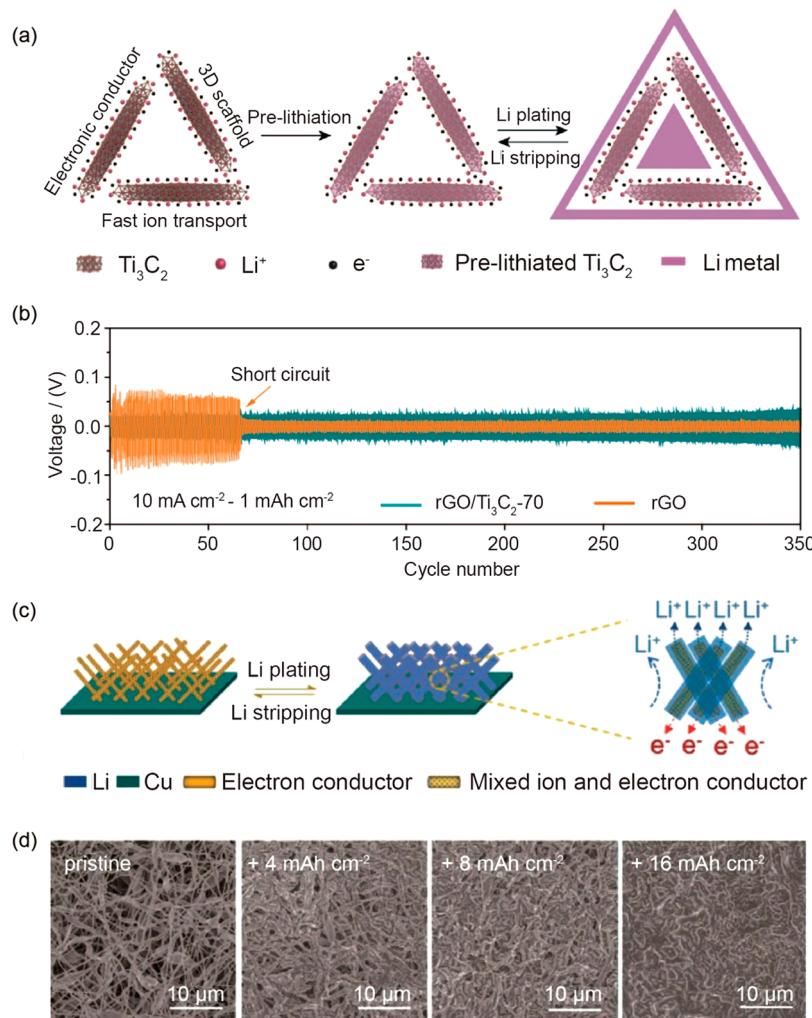


Figure 4. Dendrite regulation by controlling the Li growth pathways and directions. (a) Schematic showing MXene aerogel scaffolds with high electron conductivity and fast Li ion transport capability. (b) Long-term cycling performance of symmetric cells with MXene aerogel and pure rGO aerogel as anode scaffolds at a current density of 10 mA cm^{-2} . Reproduced with permission from ref 43. Copyright 2018 Wiley. (c) Schematic illustrating homogeneous Li plating along MIEC scaffolds. (d) Surface morphology of the pristine MIEC and scaffolds after plating different amounts of Li. Reproduced with permission from ref 45. Copyright 2018 Wiley.

should be noted that MIEC here is the abbreviation of the “mixed ionic and electronic conductor”, which is a descriptive word toward Li metal anode scaffold.

A 3D MXene aerogel was demonstrated to be an extraordinary MIEC composite scaffold for LMAs due to the high metallic conductivity and fast ion transport capability of MXene nanosheets (Figure 4a).⁴³ Li ions were calculated to have decreased diffusion barriers (0.07 eV) on Ti_3C_2 MXene sheets.⁴⁴ Therefore, an MXene-coated rGO porous structure would provide favorable Li ion transfer pathways, guide Li growth along the skeleton, and fill the voids. A small hysteresis of only 42 mV is maintained over 350 cycles for the MXene aerogel at a high current density of 10 mA cm^{-2} (Figure 4b). From the same threshold, Zhang et al. fabricated an SSE-carbon nanofiber (CNF) MIEC composite scaffold with $\text{Li}_{6.4}\text{La}_3\text{Zr}_2\text{Al}_{0.2}\text{O}_{12}$ (LLZO) nanoparticles uniformly incorporated in a CNF scaffold.⁴⁵ Li ions preferred to deposit and dissolve along the LLZO-decorated nanofibers, wrapping around the fibers until they were covered; the nanofibers then recovered their original appearance after the stripping process (Figure 4c). An obvious texture was observed under the deposition capacity of 8 mAh cm^{-2} and tended to be flat

without any protuberances until 16 mAh cm^{-2} was reached (Figure 4d). An ultralong cycling life with a hysteresis of 80 mV over 1000 h was obtained for the LLZO/CNF MIEC composite scaffold.

The 3D MIEC composite scaffold is the most representative and efficient approach to control the Li ion flux pathways and dendrite growth directions for a dendrite regulation strategy. In particular, the scaffold addressed the problems of LMAs under high current density and area capacity to provide a viable approach for safe high-rate Li metal batteries.

■ APPROACHES FOR DENDRITE ELIMINATION

Dendrite elimination is a formidable challenge and is the ultimate goal for dendrite control and the production of safe LMAs. It was explicitly demonstrated in a stress-driven dendrite growth model that filaments grow under a compressive stress. Residual stresses are pervasive during Li plating, and the presence of a critical stress is a crucial criterion for avoiding dendrite growth. How to release the stress or eliminate filamentary dendrites through mechanical force becomes a research hot spot.

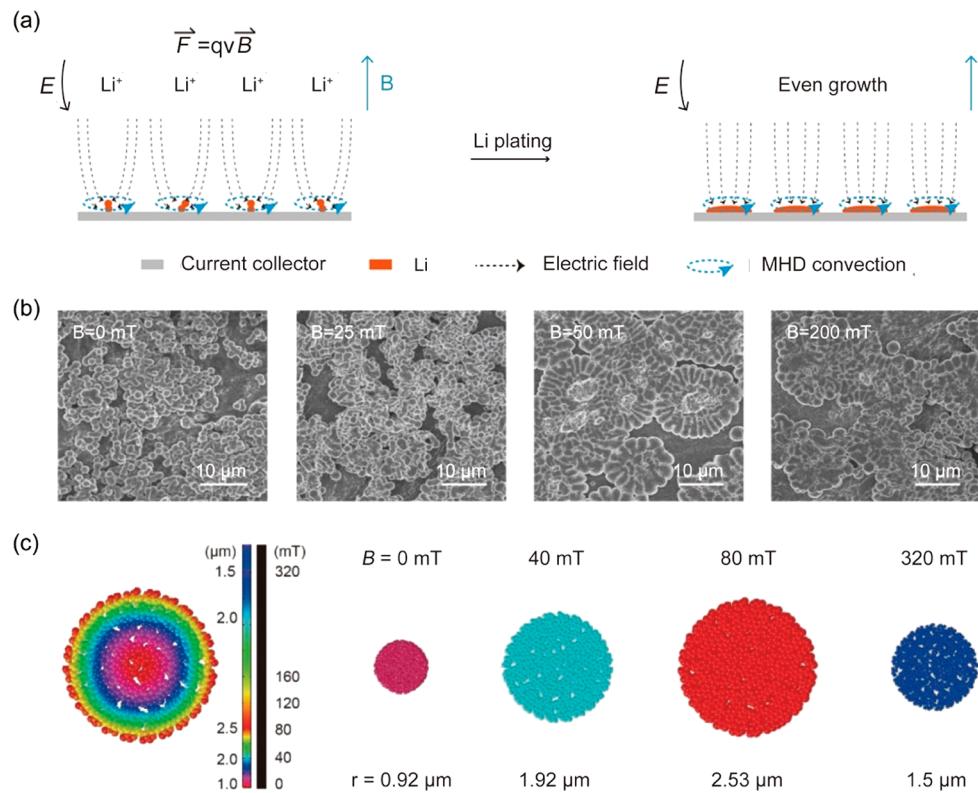


Figure 5. Dendrite elimination through Lorentz force by introducing a magnetic field. (a) Schematic showing the influence of magnetic field and Lorentz force on Li deposition morphology. (b) Morphology difference of the anode with $B = 0, 25, 50$, and 200 mT at a current density of 50 mA cm^{-2} and Li loading of 0.5 mAh cm^{-2} . (c) COMSOL finite element analysis simulation showing that the Li deposition area changed with magnetic field strength from 0 to 320 mT . Reproduced with permission from ref 48. Copyright 2019 Wiley.

Tip dendrite growth is always observed on conventional current collectors with a rough surface due to the local strengthening of the electric field.^{46,47} However, it is widely known that the migration of charged particles could be affected by the Lorentz force if the trajectory cuts the magnetic induction lines. When Li ion plates on the protuberances of substrates in a magnetic field, the electric field line deflects and intersects with the magnetic field line, causing the Lorentz force and a solution vortex (Figure 5a).⁴⁸ Dendrite tips were thus buried due to the Lorentz force. In ether electrolyte, Li tends to grow into microspheres, increase in size, and become connected with the increasing magnetic field intensity. A flattened petal-like morphology was obtained even under an ultrahigh current density of 50 mA cm^{-2} with a magnetic field of $B = 50 \text{ mT}$ (Figure 5b). This experimental observation is consistent with the COMSOL Multiphysics simulation result that the Li deposition area greatly expanded with increasing B . Once the maximum B intensity was achieved, the deposition area became inversely proportional to B (Figure 5c). No dendrite was observed at small or high current densities. The same effect of Lorentz force in eliminating dendrite growth was also demonstrated by Lu et al.⁴⁹

Electrode pulverization is another notorious problem in LMAs that always causes unevenly distributed inner stresses and substantial anode fracture. In metallurgy, bulk nanostructured materials (BNMs) with refined nanostructures are designed to release lattice stresses while enhancing the integrated yield stress.⁵⁰ This concept was adequate for LMAs. Liu et al. transplanted the concept into constructing bulk nanostructured Li (BNL) by adding trace amounts of SiO_2 into molten Li.⁵¹ Compared to bulk Li, the Li was

segmented into ultrafine grains that created large numbers of grain boundaries to alleviate the extrusion stress (Figure 6a). Dendrites were thus avoided due to the evenly dissipated stress; moreover, the enhancement of the fatigue endurance and mechanical strength prevented anode pulverization. Fractured Li and severe pulverization were obviously observed on a commercial Li foil after only 50 cycles due to the failed mechanical stress relief; however, a smooth electrode surface and integrated anode structure were retained after Li plating/stripping (Figure 6b). The volume expansion was thus self-accommodated due to the critical Li grain size. In addition, an extra grain boundary interface provided fast ionic conducting pathways and accelerated the kinetic mass transfer process.

Regardless, Li deposition in LMAs is an electrochemical process and follows the rules of conventional metal electroplating theory. Composite plating is a mature film technique to obtain an ideal cladding by co-depositing metal ions with insoluble suspended nanoparticles in the plating solution.⁵² Inspired by this strategy, we introduced 2D VSs into the electrolyte and co-deposited with Li^+ .⁵³ As illustrated in Figure 3a, surfaces of the VSs are negatively charged and thus could serve as the electrolyte additive and are colloidally dispersed in the electrolyte. An electrostatic force was quickly generated between the VS and Li^+ , and Li^+ was electrostatically absorbed onto the VS. Once the electric field was applied, substantial Li^+ -encapsulated VSs began to co-deposit onto the substrates, reducing the lateral Li diffusion barrier and forming a flake-like Li deposition layer (Figure 6c). Furthermore, after Li^+ was absorbed on the VS that deposited on the substrate, the undeposited VS was negatively charged again, returned to the electrolyte, and could absorb new Li^+ for further deposition,

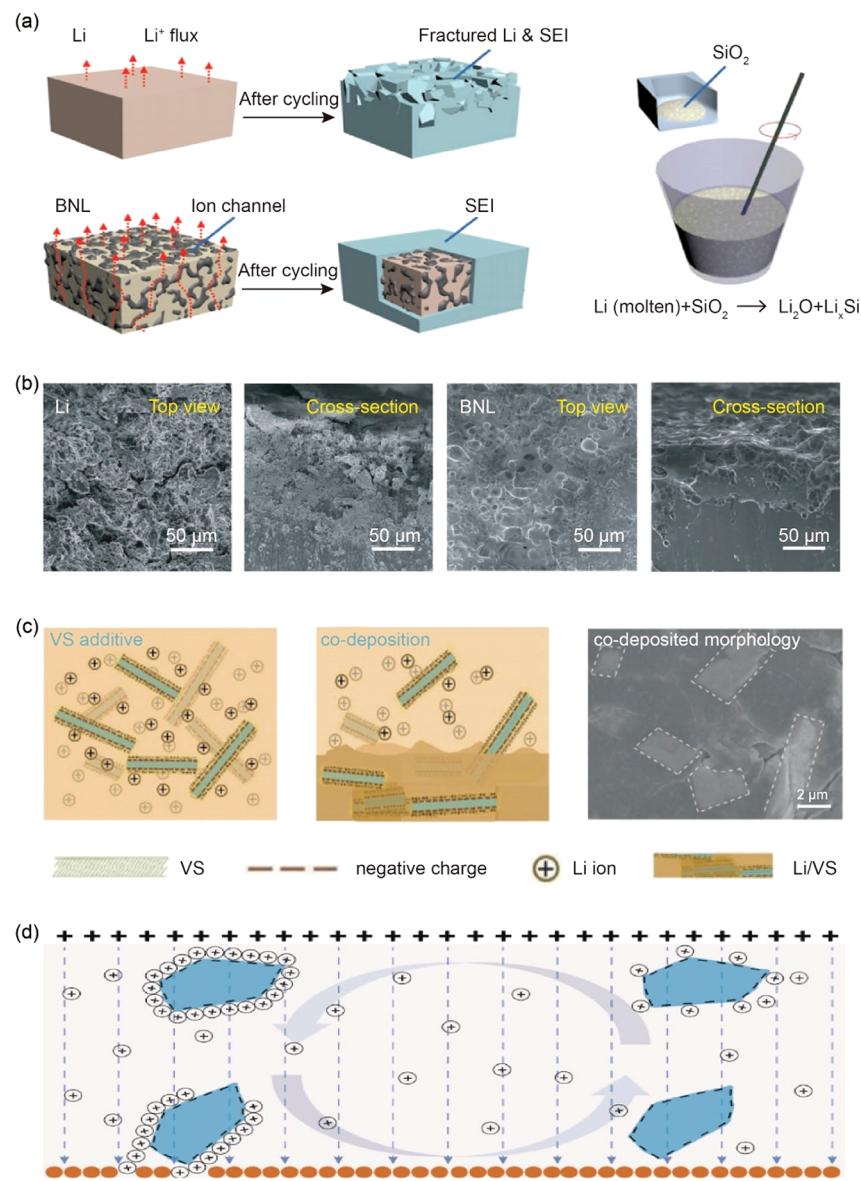


Figure 6. Dendrite elimination through enhancing the yield stress and reducing the lateral Li diffusion barrier. (a) Schematic illustration of building the nanostructured LMA with boundary stress. (b) Top view and cross-section view of pristine Li foil and Si-based BNL before and after 50 cycles. Reproduced with permission from ref 51. Copyright 2019 Wiley. Schematic illustration of (c) Li co-deposition with negatively charged VSs under electrostatic force and (d) shuttling effect of VS for homogeneous Li deposition. Reproduced with permission from ref 53. Copyright 2019 Wiley.

which is called the VS shuttling effect (Figure 6d). The anode takes advantage of the low Young's modulus of soft Li and high Young's modulus of rigid vermiculite, which was bioinspired from natural nacre and thus was called a nacre-mimetic Li anode. No dendrite can be detected for the nacre-mimetic Li anode over hundreds of cycles.

Thus, mechanical force plays an increasingly important role in fundamentally eliminating dendrite formation. Other kinds of force and more processing optimization, such as the relation between current density and force field strength, still need to be further exploited and developed for safe LMAs.

CONCLUSIONS AND OUTLOOK

To realize the final application of high energy density Li metal batteries, dendrite issues must be resolved to enable the safe use of LMAs. Several innovative strategies for dendrite suppression, dendrite regulation, and dendrite elimination

from the aspects of thermodynamic interface energy and mechanical force were discussed step-by-step in this Account. Dendrite suppression is the most basic strategy to physically obstruct growing dendrites and is thus widely used under small current densities and capacities. With the increasing demand for high-rate performance rechargeable batteries, dendrites will break through and finally penetrate the blocks under a high current density and Li loading. Dendrite regulation by controlling Li nucleation sites, Li ion pathways, and dendrite growth directions provides opportunities for high-rate operation within safe limits. For a practical LMA, a dendrite-free morphology is the ultimate goal to prevent short circuits, thermal runaway, and explosion hazards. Dendrite elimination from the perspective of mechanical force was finally explored. Other strategies for dendrite elimination are still under investigation.

In further study, breakthroughs still need to be based on the deep understanding of mechanism and process in dendrite elimination. Mechanical force regulation in affecting microstructure evolution during cycling should be characterized and investigated. Advanced characterization techniques, especially *in situ* characterization, are urgently needed to be developed to reveal the mechanism and evolution process. Materials with unique mechanical properties are also critical in eliminating dendrite formation. We hope our strategies can pave the way for safe next-generation Li metal batteries and offer promise for other metal batteries.

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Notes

The authors declare no competing financial interest.

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